# PATENT SPECIFICATION

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COMPLETE SPECIFICATION

## Paper Making

We, AMERICAN VISCOSE CORPORATION, of Philadelphia, in the State of Pennsylvania, United States of America, a Corporation organized and existing under and by virtue of the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the art of making paper from artificial fibres, in whole or in part, such as those formed from regenerated cellulose.

The art of making paper depends upon the fibrillation which occurs when paper-making fibre is beaten in water. The fibrillation manifests itself by a fraying of the surfaces and ends of the fibres in a manner to produce minute tendrils or fibrillæ which serve to felt or lock the fibres together when they are subjected to the paper-making process.

Recently, means have been found to cut regenerated cellulose fibres, such as those formed from viscose, to the prescribed paper-making length. However, regenerated cellulose fibres have not been considered as paper-making fibres due to their high swelling, softening, slipperiness, and inability to disperse in water and to fibrillate so as to hold the fibre web together sufficiently to permit its removal from the paper-making screen as a sheet. The presently employed practice of forming paper comprising regenerated cellulose fibres is to introduce the same into a previously beaten paper-making fibre of cotton, wood, manilla or other paper stock, at the beater, and without further beating other than mixing, cast them into the paper sheet with the fibrillating paper-making fibre acting as a dispersing, carrying, and bonding medium. Such sheets, however, when a substantial amount of regenerated cellulose fibres have been added, have been characterized by a high degree of porosity, softness and weakness which limit their use to restricted special applications.

Further, the use of the ordinary or conventional paper-making non-fibrous binders, bonding agents, or cements, such as glues, starches, or sodium silicate, which are applied in solution form and then dried, have not proved successful with regenerated cellulose fibres. This is probably due to the fact that conventional non-fibrous binders do not possess sufficient binding strength to cause the regenerated cellulose fibres to bind together to give the resultant sheet sufficient strength. In fact, conventional bonding agents are so lacking in binding strength for this purpose that a regenerated cellulose fibre web employing such binders is so weak structurally that the same cannot be removed while wet from the paper-making wire as a sheet.

According to the present invention, there is provided a paper sheet comprising fibrillated regenerated cellulose fibres.

The objects of the present invention are in general accomplished by beating, in an ordinary paper beater, a special high strength low elongation viscose rayon fibre, which is described in detail hereinafter, for a period which corresponds to normal paper beating time. During the beating operation the fibre remains constricted, i.e., does not swell to any appreciable extent, is reduced to paper-making length, and becomes readily dispersible. Above all the regenerated cellulose fibre fibrillates both at its ends and irregularly along its length. The beaten fibrillated fibre is then diluted to proper consistency and cast on the paper-making screen or wire and removed therefrom as a self-sustaining sheet without the addition of other fibres or bonding additives.

Ordinary regenerated cellulose or viscose rayon fibre does not fibrillate when subjected to beating in an ordinary paper beater. Consequently, the same has not

been useful as a papermaking fibre when used alone up until the present. It has now been discovered, however, that viscose rayon fibres produced as hereinafter described will fibrillate when subjected to the ordinary paper-beating operation.

Viscose which has been prepared in the usual manner is employed in making the fibrillating rayon fibre. The viscose is one which has a salt point of 3 to 6 (NaCl), cellulose content from 6 to 9%, and a NaOH content from 6 to 9%. During the process of manufacture, the alkali cellulose crumbs are aged for such a length of time so as to give a viscose having a ball fall viscosity between 65 and ~~120 seconds~~.

The viscose is passed through a spinneret into a coagulating bath to liberate the cellulose xanthate without substantial regeneration of the cellulose. The cellulose xanthate fibre thus formed is then subjected to considerable stretching which orientates the molecules in the fibre and increases the crystallinity, these two properties being determinative of the fibrillating property of the finished fibre. After stretching the fibre is passed into a regenerating bath, after which the regenerated cellulose fibre is sent directly to the usual finishing stages through which such fibres are usually passed in the normal course of their production.

Various chemical compounds may be employed in the coagulating and regenerating baths such as sulphuric acid, phosphoric acid, boric acid, acetic acid, sodium sulphate, sodium acetate, ammonium sulphate, mono- and di-basic sodium phosphate, etc.

For example, a satisfactory fibrillating viscose rayon fibre may be produced when a coagulating bath is employed having a pH in the range of 1.5 to 10 and comprising between 5 and 20% by weight of phosphate radicals and between 5 and 20% by weight of sodium sulphate, the temperature of such bath being maintained at room temperature or higher and preferably between 45 and 55° C. In conjunction with this coagulating bath a regenerating bath should be employed comprising 1 to 15% by weight of sulphuric acid. Because of the carry-over of coagulating solution in the regenerating bath by the fibre, the regenerating bath should be so regulated that it contains at all times 5 to 10% phosphoric acid and 10 to 20% sodium sulphate. The temperature of the regenerating bath is the same as that of the coagulating bath.

Fibres produced as outlined above, exhibit high tensile strengths (wet and dry) combined with low extensibilities (wet and dry) and low swellings (cross-sectional and linear) upon exposure to water or water vapour.

Average fibre properties are tabulated below:—

| | |
|---|---|
| Tenacity (Dry) | 4.5 grams/denier |
| Tenacity (Wet) | 3.0 grams/denier |
| Extensibility (Dry) | 8.0% |
| Extensibility (Wet) | 8.0% |
| Cross-sectional Swelling | 40% |
| Linear Swelling | 0.25% |

These fibres also possess the proper orientation and crystallinity that is necessary for fibrillation.

The fibre properties of other fibrillated artificial fibres will vary within the range of values tabulated below:—

| | |
|---|---|
| Tenacity (Dry) | 3—5 grams/denier |
| Tenacity (Wet) | 2—3.5 ,, |
| Extensibility (Dry) | 6—10% |
| Extensibility (Wet) | 6—10% |
| Cross-sectional Swelling | 35—45% |
| Linear Swelling | 0.20—0.50% |

In the following table there is tabulated the range of orientation and crystallinity values for the fibrillated viscose rayon fibre of the present invention as compared to those for a fibrillating natural cellulose fibre and a normal viscose rayon fibre which is non-fibrillating.

TABLE I.

| Fibre | % Crystallinity | Orientation Half maximum angle in degrees |
|---|---|---|
| Hemp | 92—96 | 12—17 |
| Fibrillating Viscose Rayon Fibre | 85—91 | 18—24 |
| Regular Viscose Rayon Fibre | 75—82 | 25—32 |

The percent crystallinity, as expressed in the table, is defined as the percent residue by weight after treatment in 2.5 normal hydrochloric acid for 15 minutes at 105—0.5° C. The orientation is expressed in terms of the half maximum angle as determined from X-ray diffraction. The half maximum angle is the angular length in degrees of the 002 interference (Miller Index) in the X-ray diagram of rayon at half the maximum intensity after a correction for background intensity. (See Ingersoll, H.G., J. Applied Physics 17, 924 (1946)).

From the values in the table, it can be seen that the orientation and crystallinity of the viscose rayon fibre of the present invention approaches that for hemp, which readily fibrillates even when the same is placed in water and stirred gently. It appears that both the proper orientation and crystallinity are necessary. That is to say that even though a fibre possesses the proper orientation, but not the proper crystallinity, or *vice versa*, it will not necessarily fibrillate. It further appears that the ideal fibre, insofar as fibrillation is concerned, would be one having 0° orientation and 100% crystallinity.

As previously pointed out, the viscose rayon fibres, produced as herein pointed out, are beaten in a standard paper beater for a period of 3 to 12 or more hours at concentrations of approximately 0.5 to 3.0%. However, when a laboratory beater is employed, a beating time of 1 to 2 hours is sufficient. The fibres fibrillate at their ends and irregularly along their lengths and disperse readily. The resultant fibrillated viscose rayon fibre dispersion may be diluted to any desired consistency, depending on the type sheet or web it is desired to produce, and cast on the paper-making screen or wire and removed therefrom as a self-sustaining sheet or web. The sheet may be formed on conventional paper-making machines of various types, such as the Fourdrinier, Harper, single cylinder or Yankee, multivat machine, mould, presse pate, or the like.

The fibrillated fibre-dispersion may be diluted to approximately 0.5 to 0.002%. For example, in making a tea bag paper, a concentration of approximately 0.002% is satisfactory, whereas in making filter paper, mineograph paper, and the like, a concentration of approximately 0.02% would be sufficient.

While the invention has been described in connection with forming a sheet or web comprising 100% fibrillated viscose rayon fibres, various other fibrillating and non-fibrillating fibres may be incorporated therewith. Also various bonding agents may be added if desired. For example, varying amounts of a fibrillating fibre may be added to the fibrillated viscose rayon fibre in the beater, such as cotton, hemp, flax, and the like. Non-fibrillating fibres such as those formed from cellulose acetate, cellulose nitrate, casein, water-insoluble cellulose ethers, etc., may be employed. The bonding agents, such as glue, cellulose ethers, and the like, may be added to the fibrillated viscose rayon fibre or a mixture of the same with fibrillating or non-fibrillating material.

Further, the fibrillated viscose rayon fibre of the present invention may be used to form sheets or webs of non-fibrillating fibres such as cellulose acetate, cellulose nitrate, ordinary rayon, etc. From 2 to 10% of the fibrillated viscose rayon fibre mixed with 90 to 98% of the non-fibrillated fibre would be sufficient to form a self-sustaining sheet on the screen or wire.

Various heat activatable, thermoplastic, or thermosetting (when in a thermoplastic state), resinous fibres may be employed with the fibrillating viscose rayon fibres. The fibrillæ of the latter enable the formation of a self-sustaining sheet or web which later may be subjected to heat and pressure thus activating the themosetting or thermoplastic resinous fibres which form a smooth, tough sheet having a high gloss making the same suitable for magazine papers and the like. Examples of thermoplastic resinous fibres are those formed from high molecular weight synthetic linear polyamides or polyesters, copolymers of vinyl chloride and vinylidene chloride, vinyl acetate, polyethylene, polyacrylonitrile, and the like. Examples of the thermosetting resinous fibres are those formed from urea-aldehydes, phenyl-aldehydes and the like. ← 3

Other shaped articles may be formed from the dispersion of fibrillated viscose rayon fibres of the instant invention. The dispersion may be applied to various shaped mandrels such as used in making hats, brassieres, and the like. This is particularly advantageous when thermosetting or thermoplastic resinous fibres are incorporated with the fibrillating viscose rayon fibres.

1 tex = 10 dtex

The fibrillating viscose rayon fibres may vary in denier from 0.75 to 5.5 and when beaten in the paper beater a fibre length between 1 mm. and 10 mm. is satisfactory. Here again the denier and fibre length will vary in accordance with the desired properties in the end product.

.01 tex = 1 dtex

1.5 dtex

The sheets or webs and other shaped articles formed from the fibrillated viscose rayon fibres have many and varied uses. For example they are useful in the manufacture of tea bags, mimeograph and overlay paper, filtering paper, papers used for wiping such as facial or toilet tissues, magazine and book paper etc. Various materials may be incorporated in the fibrillated viscose rayon fibre sheets such as dyes, pigments, various plasticizers, waterproofing agents, greaseproof agents, mildew-preventative agents, fillers, and the like.

What we claim is:—

1. A paper sheet comprising fibrillated regenerated cellulose fibres.

2. A paper sheet according to claim 1,

characterized in that said fibres are high strength, low elongation fibres.

3. A paper sheet according to claim 1 or 2, characterized in that said artificial fibres have an orientation of 18 to 24° and a crystallinity of 85 to 91%.

4. A paper sheet according to any of claims 1—3, characterized in that it comprises 90 to 98% of non-fibrillated fibres and 2 to 10% of said fibrillated artificial fibres.

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- Fib rayon
  - Primary
  - Microfibers
    - other microfibers or other fibers

2.5 - 6.5

3 - 20% fibrillated rayon { primary / microfibers <1mm at 50%

490
350
840

Non fibrillated rayon + pulp · <10mm

1350
840
510